NATIONAL INSTITUTE OF TECHNOLOGY ROURKELA

DEPARTMENT OF CHEMICAL ENGINEERING

Project Thesis Titled

Feasibility of Carbon Dioxide Sequestration in Deep Indian Coals

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CERTIFICATE

This is to certify that that the work in this report entitled **"Feasibility of Carbon Dioxide Sequestration in Deep Indian Coals"** submitted by **Shyam Sundhar S** in partial fulfillment of the requirements of the prescribed curriculum for Bachelor of Technology in Chemical Engineering Session 2006-20010 in the department of Chemical Engineering, National Institute of Technology Rourkela, Rourkela is an authentic work carried out by him under my supervision and guidance. To the best of my knowledge the matter embodied in the report is his bona fide work.

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Abstract

The feasibility of carbon dioxide sequestration in Raniganj formation coals found in and around Durgapur, West Bengal, India has been investigated. Factors like ash, moisture, fixed carbon content etc. have been found to influence the gas sorption capacity of the coal samples. It has been found that seam depth, coal maturity and sorption capacity do not have any established relationship. Samples obtained at 1079 m and 1197m showed CO_2 sorption capacity as 10.09 ml/g and 11.8ml/g respectively at temperatures of 30°C. Experimental data were verified using several adsorption isotherms such as Langmuir, BET, Dubinin-Astakhov (D-A) and Dubinin-Radushkevich (D-R) and was found to best fit D-A model indicated by minimum error. The absolute adsorbed volumes were also determined from the Gibbs values by taking into consideration the adsorbed gas density.

***Keywords*—** Adsorption, Carbon dioxide sequestration, isotherms

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NOMENCLATURE:

BET – Brunauer, Emmett and Teller adsorption isotherm

V – Total volume of gas adsorbed by a solid adsorbent expressed as mL of gas per gram of adsorbent

P – Equilibrium vapour phase pressure of the gas at the gas-solid interface

V_m – volume of gas adsorbed on the solid surface for monolayer adsorption expressed in mL

V_o – D-R or D-A adsorption isotherm constants

psi – unit of pressure, pounds per square inch

P_o – saturated vapour pressure at a particular temperature

m^3/t – cubic metre per ton

D – D-R or D-A parameter corresponding to pore size distribution

R – Universal gas constant

T – Absolute temperature

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1. **INTRODUCTION**

Introduction:

In the current scenario of climate change the most debated are the effect of green house gases (GHGs). Among these gases, the effect of carbon dioxide or CO_2 has been estimated to be of highest concern due to its shear concentration in the atmosphere. This has been looked upon from two perspectives-one being the reduction of CO_2 emissions to the atmosphere and the other one being reducing the present concentration of CO_2 in atmosphere to safe levels through application of various engineering principles, sequestration being one such principle.

Sequestration is the process of capturing any gas and storing that gas permanently in any media. Capture of CO_2 and its storage is either termed as carbon capture and storage (CCS) in general or CO_2 sequestration in particular. CO_2 has a lot of possible media for its permanent storage like depleted oil and gas fields, saline formations, unmineable coal seams and saline filled basalt formations. When one of the above media is involved, it is specifically termed as geo-sequestration. Sequestration has been proposed as one of the means of mitigation of CO_2 emissions from large point sources (LPSs) [1].

In the Indian context, the soaring power demand will necessitate tripling installed generation capacity from 101,000 to 292,000 MW over the next two decades, much of it derived from poor quality coal. Coal contributed to about 50.8% of our fossil fuel consumption till 2005 [2]. Similar demand increases are forecast for all fuels, and resultant CO_2 emissions from LPSs are projected to increase from 1229 Mt to 3084 Mt by 2030 [2]. One of the mitigation techniques suggested for CO_2 emitted by LPSs by the IPCC is CO_2 sequestration.

India being a coal rich country has about 10% of world reserves standing third next only to the USA and China [2]. This accounts only for the mineable part of the reserve. One of the main ideas behind this study is to use the unmineable coal seams of Gondwana origin at depths below 800m as sinks for CO_2. Apart from sequestering CO_2, extraction of methane (CH_4) from the coal bed can also be done simultaneously because, of the fact that coal has a higher affinity for CO_2 than for CH_4 [3]. The CH_4 so obtained from the coal seams is called coal bed methane (CBM). The use of CO_2 to enhance methane production is being studied and is termed as enhanced CBM (ECBM).

A preliminary study of the Raniganj basin around Durgapur was carried out to test its sequestration potential. The basin was also one of the regions that had ongoing ECBM projects taken up by Essar explorations and productions India Ltd (EEPIL). This study has focussed only upon the adsorption characteristics of CO_2 on these coals while a complete sorption study of both CO_2 and CH_4 are required for this purpose.

2. **MATERIALS & METHODS**

2 Materials & Methods

2.1 Coal samples and preparation:

Coal samples obtained from Raniganj East CBM Block through EEPIL was Gondwanna coal from the Permian age as illustrated in (Table 2-I). Samples were obtained from 3 bore holes of EEPIL. Two samples were obtained from each bore hole from different depths as followed by Hajra in [4].

The crushed samples of the coals were ground to pass through a sieve of size 72 BSS mesh. Subsequently, the powdered samples were moisture equilibrated in an environmental chamber at the experimental temperature and 96% humidity. The moisture content of the samples as received was determined as per the standard test method for equilibrium Moisture of coal [ASTM D 1412 – 93]. Both proximate and ultimate analysis of coal samples were performed as per the standard methods [ASTM D3172-07a ; ASTM D3176-09] [5].

Table 2-I: Coal samples and Location

Sample Number	Drill Hole	Depth (Range in m)	Lithotype
S-1	EDC #4	1197.0-1197.3	Bright
S-2	EDC #4	631.00-631.24	Bright
S-3	EDC #14	982.06-982.26	Dull
S-4	EDC #14	864.71-864.98	Bright
S-5	EDC #13	1079.40-1079.70	Bright

2.2 Experimentation:

CO_2 sorption testing was performed with a self fabricated apparatus which is described below. Sorption was measured for a maximum CO_2 pressure of 800 psi.

2.2.1 Sorption Apparatus:

Detailed description of the apparatus and the procedure for gas measurement is mentioned by Harpalani in [6], though a pictorial representation of the apparatus is shown in

figure 1. The exact picture of the equipment has been shown in figure 2 & 3. The pressure transducers were connected to Data Acquisition System (DAS). The adsorption data were collected through the DAS with compatible software installed on a PC.

2.2.2 Procedure:

The volumetric apparatus was kept immersed in a constant temperature water bath maintained at uniform temperature. The adsorbed volume was determined at constant temperatures as a function of pressure at equilibrium. Equilibrium at each isotherm point is assumed to have been reached at a constant pressure after 8 hours. Real gas law was applied to determine the gas adsorbed. Peng-Robinson Equation of State was used to calculate the compressibility factor in the real gas equation. The fixed volume and the void volume were determined through helium expansion. Correction for the gas adsorbed at each isotherm step was accomplished assuming the liquid density of the adsorptive. After conducting the experiment at a fixed temperature, the sample was depressurized. The temperature of the water bath was maintained at the fixed temperature and the process was repeated for adsorption study with the new samples.

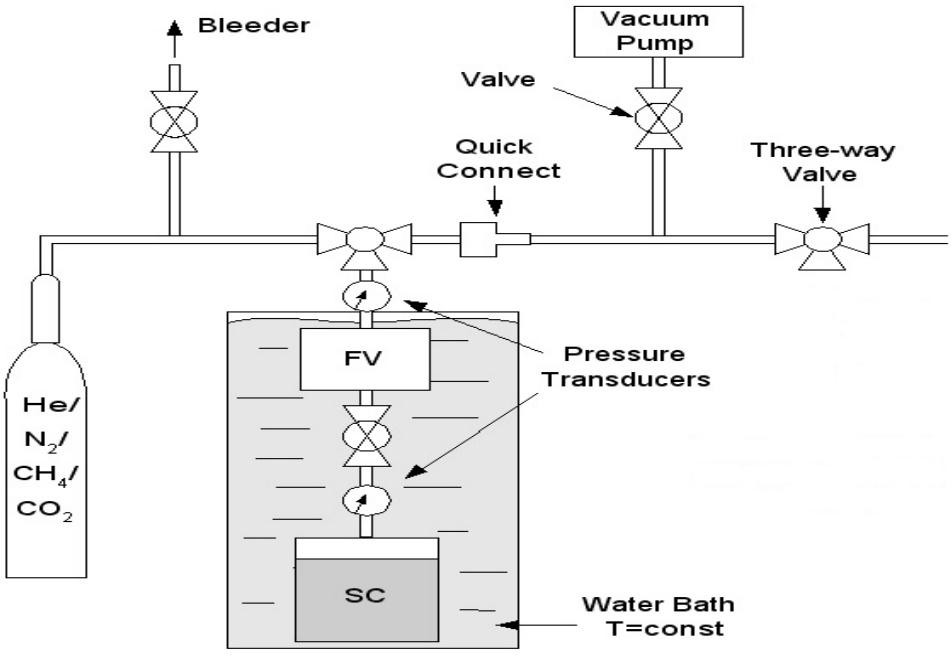

Figure 2-1: Line diagram of fabricated setup

The FV represents the reference gas chamber; SC, the sample chamber; PT refers to the pressure transducer used to measure the pressure at the openings of the sample as well as the reference chambers. A micro-filter (not shown in the figure) was also included between the sample chamber and the first pressure transducer to prevent loss of specimen during the application of vacuum.

2.3 CO_2 sorption calculations:

The quantity of gas adsorbed was calculated through difference. The volume of the empty sample and reference cells were calculated using helium gas through difference. Subsequently, the void volume of the sample is calculated by purging the sample with helium prior to purging it with CO_2. The amount of gas adsorbed by the sample is determined from the difference between the quantity of gas supplied and the quantity of gas that is present in the free space. The calculations performed were similar to those performed by Sakurovs in [7].

2.4 Modelling carbon dioxide adsorption data:

Different isotherm equations of the likes of Langmuir, BET, D-R and D-A were used to create models to correlate the adsorption data obtained for CO_2. Langmuir model equation was used to obtain the Langmuir constants V_m and k. These values were utilized to establish the Langmuir isotherm. The direct estimation of its vapour pressure is practiced as the experimental temperature for CO_2 being below its critical temperature[1]. The vapour pressure value obtained was used in BET equation to obtain the monolayer coverage (V_m) and BET constant(C). These constants helped to predict the BET isotherm. Similarly, estimated vapour pressure for individual gases was utilized in D-R equation to obtain the micropore volume (V_o) and the constant (D) that predicted the D-R isotherm. D-A equation comprising three parameter, the micropore volume(V_o), constant (D) and structural heterogeneity (n) were obtained using the measured data and estimated vapour pressure to predict the D-A model isotherm. The description of the above isotherm models is given below.

[1] The critical temperature of CO_2 is 31.1^{o}C or 304.1K. The experiments were carried out at a bath temperature of 30^{o}C or 303K.

Figure 2-2: Experimental setup

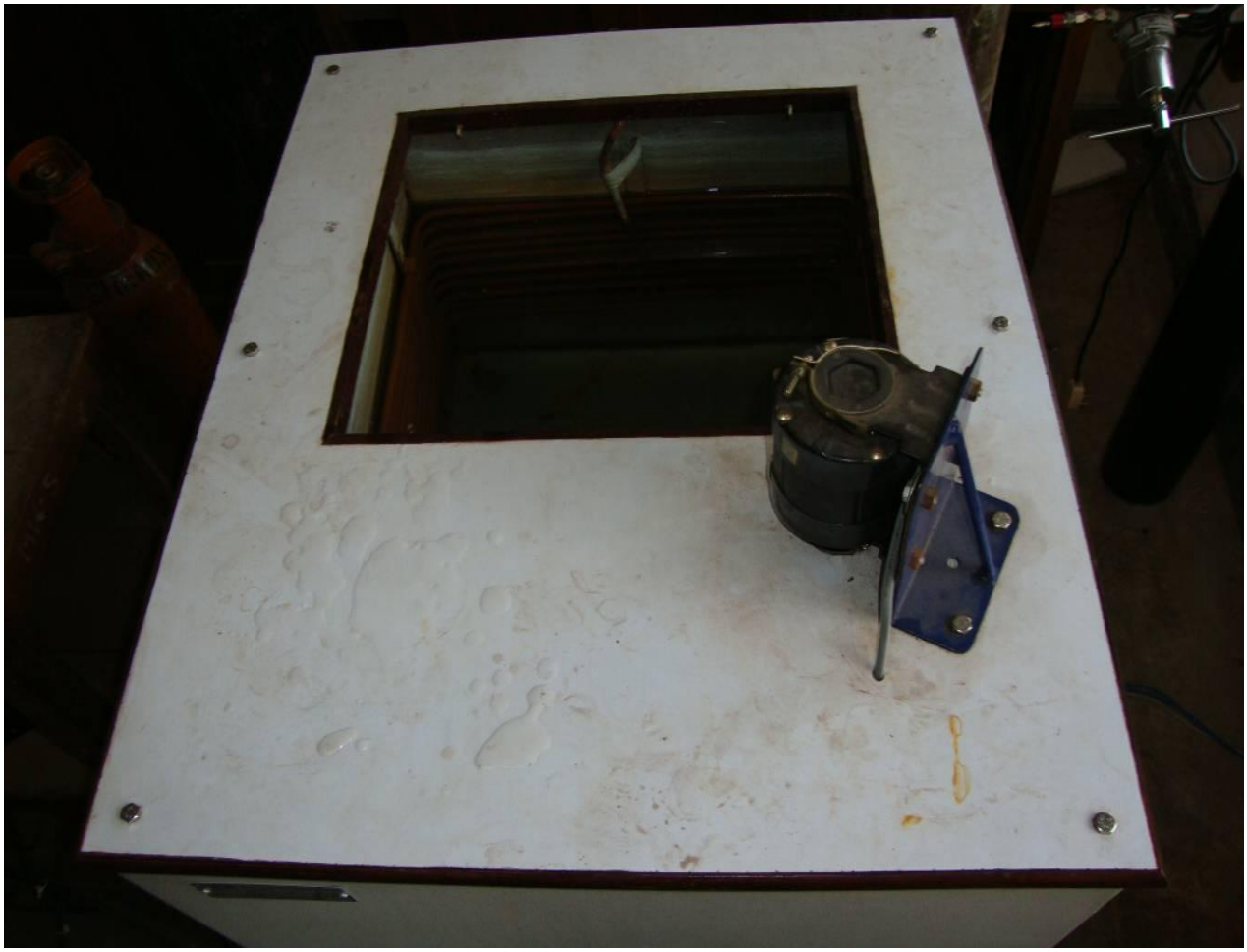

Figure 2-3: Temperature bath of the experimental setup

2.4.1 Langmuir adsorption isotherm:

The Langmuir equation [8, 9] as shown in equation (i) was derived by Langmuir for the monolayer adsorption of gases on solids. This equation relates the volume of gas adsorbed on the solid surface to the amount of gas/partial pressure of gas in the gas phase. Thus, according to this relation the amount of gas adsorbed on any solid is a function to the quantity or pressure of the gas in the gas phase.

$$\frac{V}{V_m} = \frac{kP}{1+kP} \qquad \textbf{(2.1)}$$

This equation is applicable only for the case of porous solids and represents a Type-I isotherm. The above equation gives the average number of bound molecules *V*, per number of sites on the surface, V_m, at equilibrium. The energy of interaction between the adsorbing molecules and sites on the surface is denoted by a constant *k*. This equation can be modified by replacing *1/k* with P_L and represented as

$$\frac{V}{V_L} = \frac{P}{P_L + P} \qquad \textbf{(2.2)}$$

where *P* is the equilibrium pressure; *V* is the adsorbed volume; V_L is the maximum monolayer volume that shows the maximum sorption capacity of coal; *k* is the empirical constant that represents the measure of curvature of the isotherm. The above equations are limited to monolayer coverage on the pore walls and the isotherm plateau relates to completion of monolayer Langmuir model. P_L signifies the pressure to which the coal bed reservoir has to be depleted to achieve 50% recovery. There are numerable literatures that show Langmuir equations to fit well over the range of temperature and pressures [6].

2.4.2 BET adsorption isotherm:

Brunauer, Emmett and Teller (BET) model extends the Langmuir model to multilayers [8, 9]. This equation for n layers of gas adsorbed on the solid surface is given below as in equation (iii).

$$\frac{V}{V_m} = c\left(\frac{P}{P_o}\right)\frac{[1-(n+1)(\frac{P}{P_o})^n + n(\frac{P}{P_o})^{n+1}]}{[1-\frac{P}{P_o}][1+(c-1)(\frac{P}{P_o}) - c(\frac{P}{P_o})^{n+1}]} \qquad \textbf{(i)}$$

The above equation when reduced for monolayer adsorption where *n=1* is given below. This reduced form was used to model the adsorption data of CO_2 on coal.

$$\frac{1}{V(P_o/P-1)} = \frac{1}{V_mC} + \frac{C-1}{V_mC}\frac{P}{P_o} \qquad \textbf{(2.4)}$$

Here, V_m is the monolayer volume of gas adsorbed on the solid surface; P is the gas phase pressure; P_o is the saturated vapour pressure under experimental temperature conditions. The saturated vapour pressure is at a given temperature, the maximum partial pressure that the vapour molecules would exert at saturated condition. This vapour pressure is calculated using Antonie equation whose constants where obtained from [10].The rate of multilayer formation is directly proportional to the constant C. Though this equation fits rarely to the adsorption at supercritical conditions; still it is considered to be a useful tool in case of quantitative analysis. The model is valid between relative pressure values (P/Po) of 0.05-0.35 [11].

2.4.3 Polanyi's potential theory:

The Potential theory, as postulated by Polanyi in [12, 13], assumes a potential field in the vicinity of the adsorbent surface to which the gas molecules get adsorbed and has a definite adsorbed volume. The adsorption potential is defined as the work done per mole of adsorptive in transferring molecules from the gaseous state to adsorbed state and represents the work done by temperature-independent dispersion forces. The potential curve is not dependent on temperature and is characteristic of the particular gas-solid system only. Based on this theory, Dubinin proposed in [14] a simple functional relationship between the volume adsorbed in the micropores, W, and the adsorption potential, A and represented as:

$$W = W_0 \exp(-KA^2) \qquad \textbf{(2.5)}$$

Where W_o represents the maximum volume adsorbed in micropores and K is the characteristic parameter for the gas-solid system. The above equation was modified as:

$$W = W_0 \exp(-(\frac{A}{E})^2) \qquad \textbf{(2.6ii)}$$

Where E, the characteristic energy parameter, depends on the properties of both the adsorbent and adsorptive; Conventionally, E is assumed as equal to βE_o where E_o represents the effect of adsorbent obtained with reference as benzene with $\beta = 1$ and β is called the affinity (similarity) coefficient that accounts for the effect of adsorptive. E_o is otherwise known as the characteristic energy [15]. The above relationship, known as Dubinin-Radushkevich (DR)

equation, was the initial step towards extensive studies that led Dubinin to formulate so-called theory of volume filling of micropores (TVFM) that is based on the concept of enhanced pore pressure. It describes adsorption in micropores as a process, where gas phase molecules are drawn into the interior of the micropores. On gas compression, they are further pressed interior into the pores by overlapped potential forces. If the pressure is beyond the corresponding vapour pressure, the adsorbed phase turns into liquid. Thus it is believed that in the micropores, due to enormous enhanced pressure, adsorbed phase exists in the liquid form even at low bulk pressure. However, DR model equation could not adequately describe the experimentally adsorbed data on adsorbent . Hence, to overcome this difficulty, Dubinin & Astakhov in [16] proposed a 3-parameter D-A equation in the following form:

$$W = W_0 \exp(-(A/\beta E_o)^n) \qquad \textbf{(2.7)}$$

Where n is the empirical heterogeneity parameter, used as macroscopic measure of the sharpness of micropore size distribution. For solids with relatively narrow micropores, D-A equation with n equal to 4 describes the experimental data well. Thus, if n deviates from 4, the sorption is assumed to be heterogeneous or believed to consist of wide micropore size distribution. The adsorption potential A is defined as the change in Gibbs energy with a negative sign [15].

$$A = -\Delta G = RT \ln(p_o / p) \qquad \textbf{(2.8)}$$

The D-R and D-A equations described above are further deduced in terms of measurable quantities and model parameters. The D-A equation in its reduced form is given by equation (2.9) and the D-R equation is given by equation (2.10). Thus, from the said relations it can be seen that the D-A equation reduces to a the D-R equation when the parameter value of *n* is equal to 2. The D-A equation is only valid for the condition of $1 \le n \le 4$.

$$V = V_o \exp(-D(\ln \frac{P_o}{P})^n) \qquad \textbf{(2.9)}$$

$$V = V_o \exp(-D(\ln \frac{P_o}{P})^2) \qquad \textbf{(2.10)}$$

Here, V_o is the micro-pore filling capacity; D is the pore size distribution parameter of the adsorbent and V is adsorbed volume.

3.RESULTS & DISCUSSIONS

3 Results & Discussions:

3.1 Geochemistry:

Though the class and rank of coal were known to be high volatile sub-bituminous coal the proximate analysis were performed in order to estimate the amount of CO_2 adsorbed by on dry ash free (daf) basis. The estimation of volatile matter was done in order to understand the relation between volatile matter content and the adsorption potential of coal, if any existed.

Table 3-I: Proximate & Ultimate analysis results

Sample No.	Volatile Matter, %	Ash, %	Moisture, %	Fixed Carbon, %	Ultimate Carbon, %	Hydrogen %	Nitrogen %	Sulphur %
S-1	37.0	12.0	0.6	50.4	89.73	3.097	6.93	0.243
S-2	27.0	37.0	3.2	32.8	88.89	4.605	6.24	1.559
S-3	37.0	22.0	1.0	40.0	90.01	4.485	5.29	0.215
S-5	41.0	9.0	1.0	49.0	88.84	4.79	6.17	0.203

Proximate Analysis results showed ash contents varying between 9% and 22% except for one sample that showed an abnormally high ash content of 37% (Table 3-I). No such anomalies were seen in values of either volatile matter content or moisture content. Though Indian coals are said to have very high ash contents with a mean value of around 44% [2], in this case the coals from Raniganj had very low ash and moisture contents than normal Gondwana coals as said by Hajra in [4]. This indicates the superior quality of coal. Generally it is established that the fixed carbon content of coal increases with increase in depth which is directly proportional to coal maturity [4], this is evident from the results obtained for Indian coals (Table 3-I). The history of formation and the geological processes that lead to the current Gondwana coals of India in general have been discussed in [17].

Literature suggests that the Gondwana formation in the Raniganj fields was formed from deposition of glacial and pre-glacial sediments of the Talchir formation. This has been discussed in detail elsewhere [17].

3.2 Adsorption capacity:

The amount of gas adsorbed was determined using the above described apparatus and procedure and is given in Table 3-II. The variations parameters affecting the adsorption capacity of the sample have been discussed in the subsequent sections of the text. The total CO_2 adsorption capacity of the sample is calculated as the maximum CO_2 adsorbed by the sample under the highest pressure of CO_2 to which the sample is subjected on daf basis.

Table 3-II: CO_2 sorption capacity of Raniganj coals

Sample No.	CO_2 adsorbed (mL/g)
S-1	11.86
S-2	5.15
S-3	8.35
S-5	10.09

3.3 Moisture effects on adsorption capacity:

The water present in coal is said to hinder its adsorption capability of all gases [18]. This is because of the fact that water competes for spaces in the coal matrix that could have acted as the surface of adsorption for the gases and also prevents gas access to micro-pores. Inherent moisture is the main control on the adsorption capacity and is found to be the dominant controller, [19]. It has been reported that coal sorption capacity increases with decrease in inherent moisture content. Though variations in sorption capacity with moisture have been studied for Australian coals [20] and US coals [21], there has been no such dedicated study made as regards to the Indian coal typically for Raniganj formation. General observations for these coals has been that there is a remarkable decrease in sorption capacity with increasing moisture up-to a certain moisture content beyond which there is no significant effect of moisture on CO_2 adsorption. This value is usually termed as the equilibrium moisture content. The decrease in

sorption capacity with increasing moisture content can be explained by TVFM. The moisture present in coal occupies micropore spaces in coal thereby forcing CO_2 molecules to compete for space within the pores. This fact has been explained in [20, 21]. Moreover, Levy [20] also states that equilibrium moisture content passes through a minimum for high volatile bituminous rank range coals and Raniganj coal agrees to this fact. It is evident from our observations that coal adsorption capacity increases with reducing moisture content. It is also seen that the moisture content varies between 3.2% - 0.6% for increasing coal depth. From the above observations it can also be said that the micropore structure is disturbed by the presence of water molecules in the microporous matrix. Expansion of the pore during drying of moisture might result in increasing sorption capacity [22]. This eventually may lead to non-satisfaction of the TVFM proposed by Polanyi in [12, 13]. It has also been concluded in [22, 23] that the swelling contributes to a significant reduction in sorption capacity of the coal investigated. Thus, it can be summarised that the presence of moisture affects sorption in coal in the following ways, (a) pore blockage, (b) gas dissolution, and (c) structural changes due to coal swelling.

3.4 Effect of ash on adsorption capacity:

Ash in coal is generated from mineral matter present in coal. This is generated from the fossils from which coal is formed. Ash essentially does not serve as a site for adsorption of any of gases in coal but rather acts as simple diluent. As evidenced from Table-2 the ash content of coal at depth 631 m is 37% which is much greater than the coal samples obtained at depth > 982m . It is also seen that coal samples at depth ranging 1079m-1197m show very little variation of ash content (3%). It is evident from the CO_2 adsorption study that adsorption capacity varies by 1.77 ml/g for the above mentioned coal samples. Thus, essentially a coal with higher ash content has reduced area covered by the micropore structures. This essentially decreases the sorption capacity of the coal. Similar findings have been reported for Canadian coals [24]. One of the facts behind the above explanation is that the micropore structure of coal is formed from the combustible hydrocarbon constituents of the fossils from which coal is formed. The structure of the micro-pore depends on the age of the coal seam and hence the fossil itself. The micropore structure is more developed in case of highly mature coals. The mineral matter in coal may or may not interact with the hydrocarbon part of the structure. In cases where negative interactions

are present this may affect the structure of the micoporous matrix thus decreasing the sorption capacity. This is because of the fact stated by [25] that the pore structure of coal is strongly influenced by the presence of hydrogen atoms bound directly to carbon atoms. At the same time the effect of CO_2 injection on the pore structure has also been found to be negligible by [25] who state that, the pore structure of coal measured by CO_2 adsorption is not affected by the presence of hydrogen atoms in the form of O_2 containing functional groups.

3.5 Effect of seam depth on adsorption capacity:

Coal rank is said to increase with increase in coal maturity and hence coal depth. This fact has been supported in case of American coals by Lakshminarayana [26]. It is also true in case with the Raniganj formation [Table 2-I]. Coal maturity and hence ash, volatile matter and moisture also seem to have a definite relationship with coal seam depth. Effect of coal rank on gas adsorption capacity has been studied by Clarkson [24] for Canadian coals for both CO_2 and methane. Though the volatile matter content appears to increase with increase in depth from sample S-2 through S-3, this relation is not well supported in case of movement from specimen S-5 to S-1. One of the reasons could be that, due to the inherent heterogeneity of coal the composition of coal could vary from bore hole to bore hole as samples S-1 and S-5 come from different bore holes along the same seam. At the same time this very explanation fails in case of specimens S-2 and S-3 which were also obtained from different bore holes along the same seam. Though the adsorption capacity of coal has a definite increasing trend with increasing seam depth, there seems to be no definite relation of adsorption capacity with the volatile matter content. Apart from the relation with volatile matter content there seems to be no anomaly to the fact that adsorption capacity increases with increase in coal maturity. This is further substantiated by the increasing adsorption capacity with fixed carbon content (Table 3-I).

3.6 Langmuir adsorption isotherm:

The experimental data was used to model the adsorption kinetics on the basis of the Langmuir model through equation (2.2). The Langmuir m parameters were estimated using linear regression analysis of the experimental data and have been listed below (Table 3-III). The comparison between experimental and parametric Langmuir models has also been shown (Fig. 3-1).

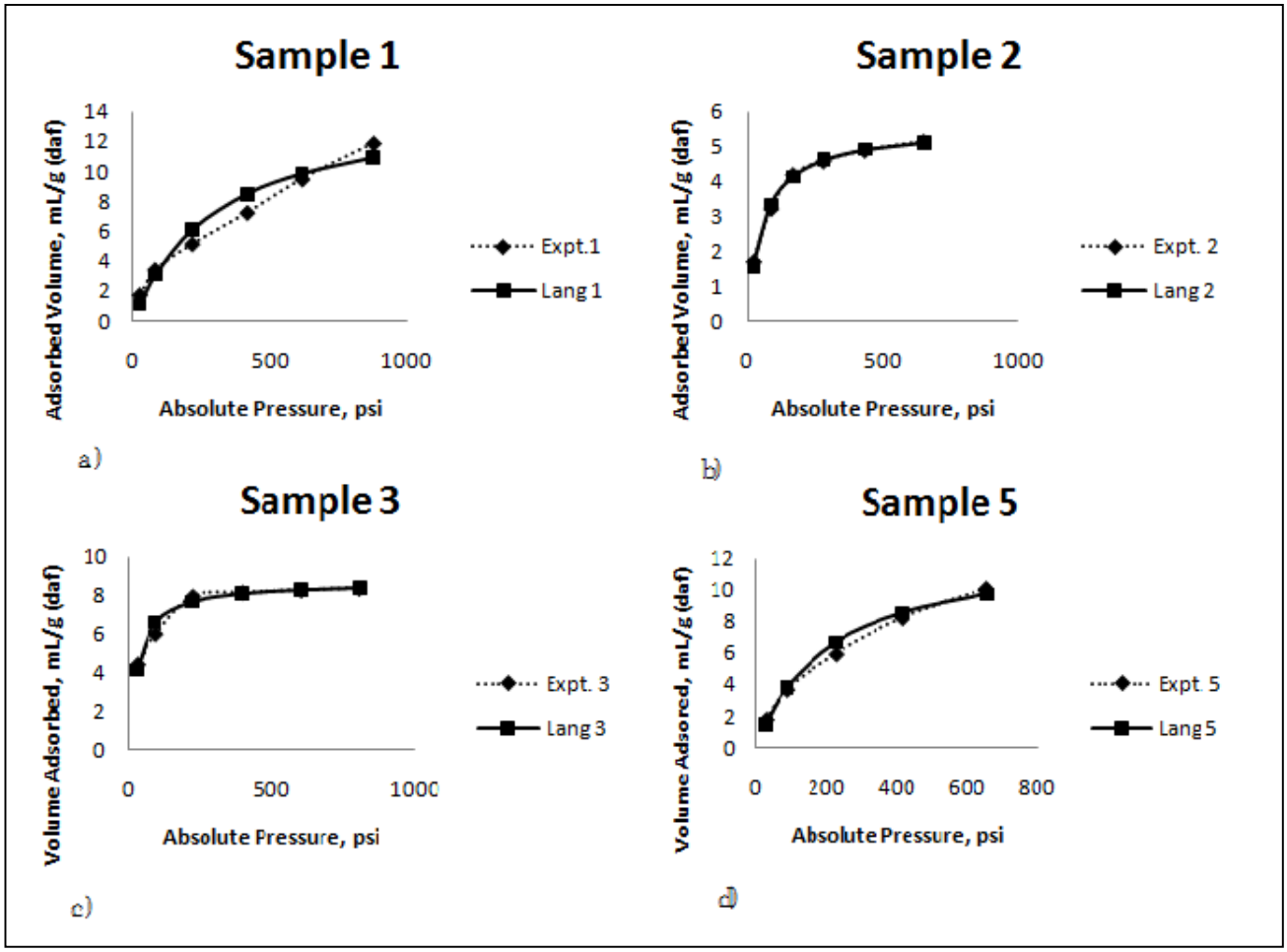

Figure 3-1: Comparison between Langmuir & experimental values for 4 samples at 30°C

Though the langmuir model satisfies the experimental results to some extent deviations from the models exists to a larger extent for S-1 and S-5 which have considerably higher sorption capacities than their counterparts. In both cases the langmuir model fails to predict the sorption capacities at higher pressures and delivers a lower value than that is seen experimentally.This can be accounted by the fact that langmuir, that gives a similar trend (Fig. 3-1) do not account for the gas adsorbed in the micoporous structure of the coal matrix. Since langmuir and BET models account only for monomolecular layer adsorption on the surface, the resultant adsorbed volume given by these models is much lesser. But, the fit for specimens S-2 and S-3 is very perfect as seen from the %ARE values that has been shown in a later section. Though pressure are high in

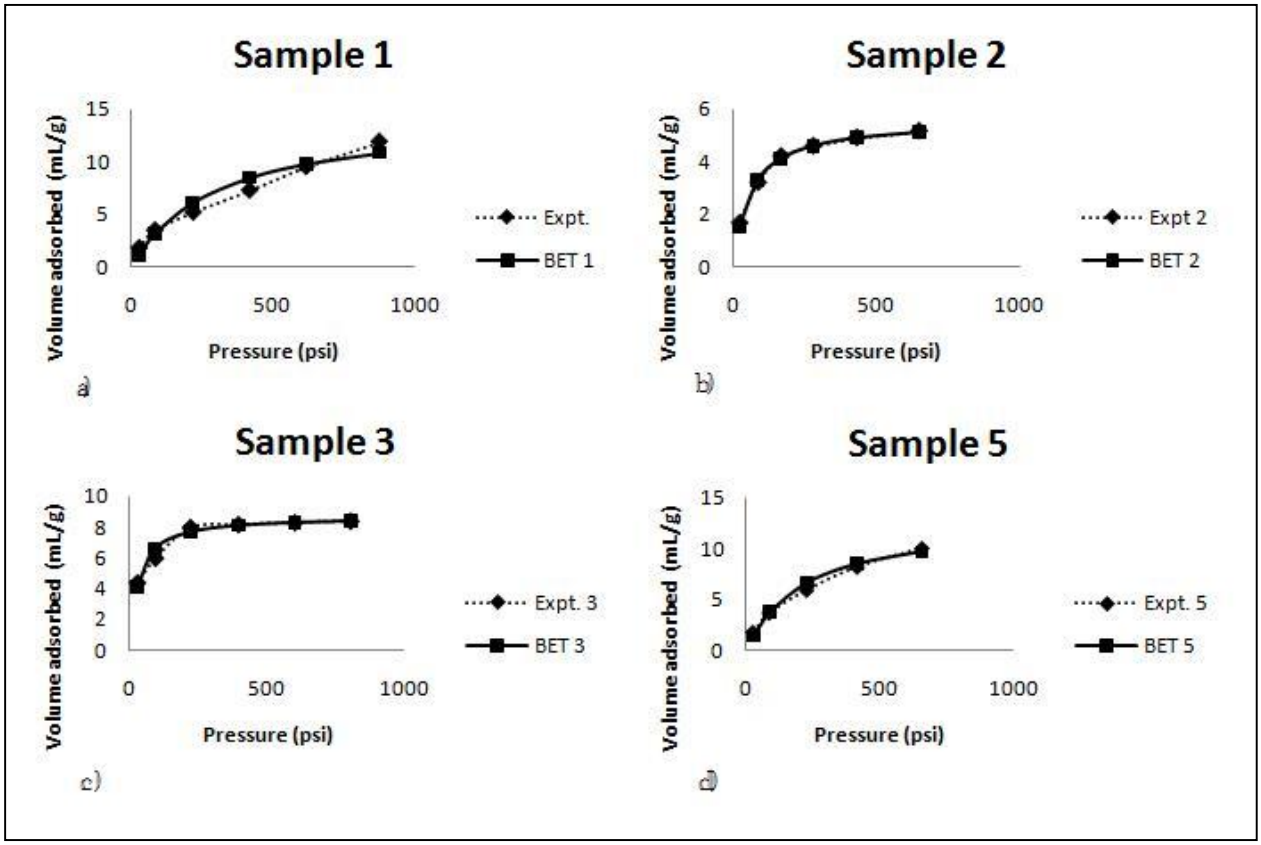

Figure 3-2: Comparison of BET model and experimental values for 4 samples at 30°C

this case the adsorption capacity is lower as compare to the other two samples. This also explains that monolayer adsorption is dominant in these two cases. The BET model also gives similar results and the plots are shown here (Fig. 3-2). This can be explained by the fact that the BET model has been considered from the simplified equation (2.4) rather than equation (2.3) for multi layer adsorption.

Table 3-III: Langmuir adsorption isotherm parameters

Langmuir constants	**S-1**	**S-2**	**S-3**	**S-5**
K	0.0033	0.0168	0.0338	0.0048
V_m (mL)	14.71	5.59	8.70	12.82

3.7 D-R and D-A adsorption isotherms:

The D-R and D-A parameters are given in tables 3-IV & 3-V respectively. While the D-R parameters were estimated through linear regression analysis, the D-A parameters were estimated using non-linear regression using SPSS 13.0 from equation (2.9) and (2.10). The comparisons for both D-R and D-A have been shown (Fig. 3-3 & 3-4). This suggests that though the D-R equation adequately represents the data for S-2 and S-3, it is not able to do so for S-1 and S-5. This again suggests that the parameter value of n = 2 in the Polayni's potential theory is not suitable enough to represent the presently available experimental data. The study of the D-A parameters, which was estimated with a limiting constraint $1 \le n \le 4$, suggests that n varies between 1 and 1.5 for S-1 and S-5 while for S-2 and S-3 it is close to 2 suggesting why D-R represents these samples more accurately. Since, the parameter n is greater than 2 for both cases it also suggets that D-R may fail at higher pressures for these samples too. This furthet substantiates the fact that monolayer adsorption is prominent in cases of S-2 and S-3 while TVFM is capable of explaining the adsorption behaviour of S-1 and S-5.

The validity of the D-A model even under higher pressures can be seen from the plots of equilibrium pressure against the volume of gas adsorbed at that equilibrium pressure. Moreover, D-A is capable of representing all specimens perfectly, including those for which Langmuir was a better fit. This helps in understanding the fact that the potential theory proposed by Polanyi in [12, 13] is in fact even capable of explaining monolayer adsorption in terms of adsorption in micropores through TVFM. A comparison between the D-R and D-A parameters reveals that for S-2 and S-3 as n in D-A is closer to 2, the values of D and V_o for both D-R and D-A are approximately closer to each other. This is in accordance with the basis with which D-A isotherm was formulated with D-R as the basis.

Table 3-IV: BET model parameters

Constants	S-1	S-2	S-3	S-5
C	4.632	18.900	39.333	6.267
V_m	11.364	5.291	8.475	10.638

Table 3-III: D-R model parameters at 303K

Constants	S-1	S-2	S-3	S-5
D	0.124	0.078	0.050	0.121
V_o	8.980	5.280	8.482	8.989

Table 3-IVI: D-A model parameters at 303K

Constants	S-1	S-2	S-3	S-5
n	1	2.125	2.102	1.143
D	0.562	0.066	0.044	0.422
V_o	12.979	5.206	8.461	12.160

The original D-R equation given by equation (2.10) was used here as the experimental conditions where below that of critical point. For experiments carried at temperatures and pressures above the critical point a modified D-R equation has been proposed by Sakurovs in [27]. Apart from these studies there isn't sufficient literature to support the present case with Raniganj coals in India. But, Day has conducted various sorption studies for various Australian and New Zealand coals in [7] using the D-R and modified D-R equation. He has proposed in [7] that the sorption capacity of these coals is much independent of the maceral compositions and highly dependent on the seam depth and hence coal maturity.

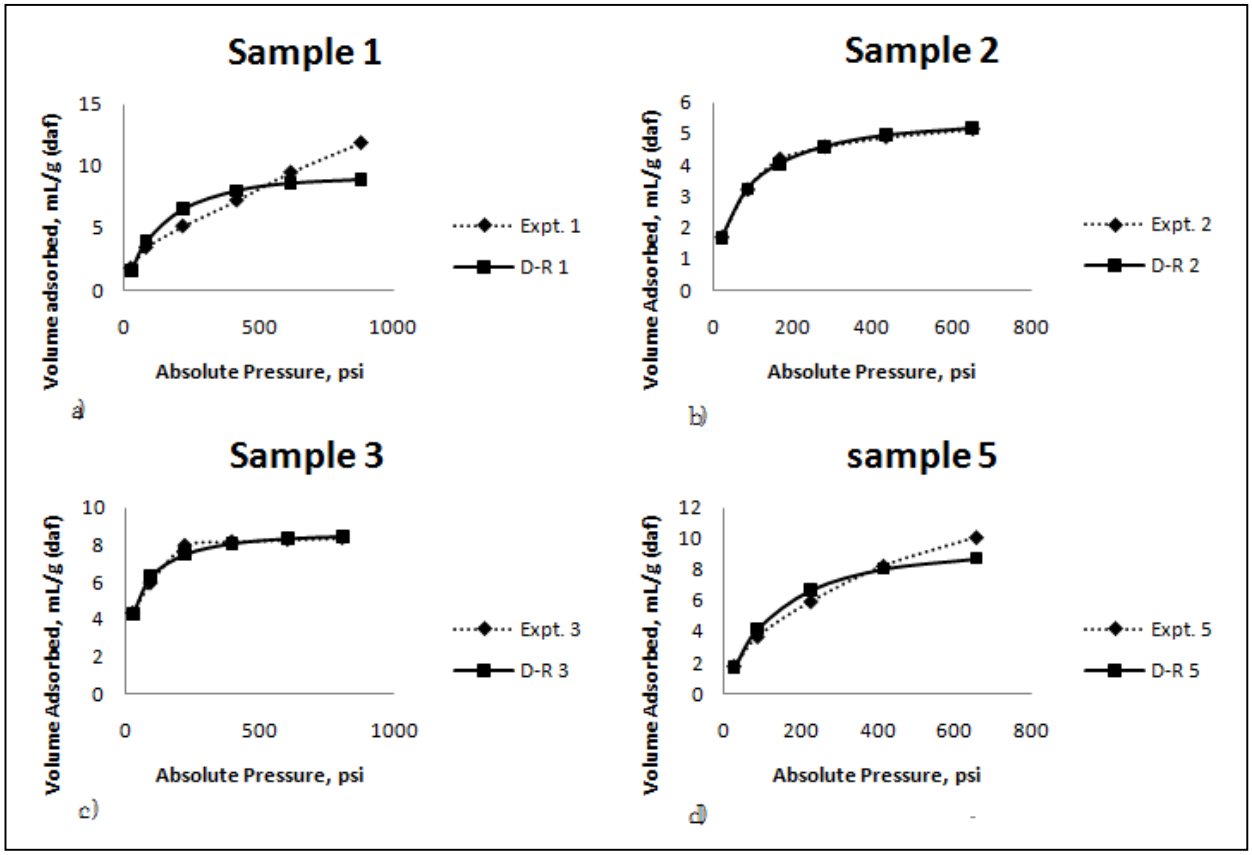

Figure 3-3: D-R model adsorption curves for 4 samples at 30°C

3.8 Absolute Residual Error:

The percentage of Absolute Residual Error (ARE) was used to calculate the percentage deviation of the experimental results from the theoretical models discussed above. The percentage error was calculated using the following equation.

$$\%ARE = \frac{\sum_{i=1}^{j} abs(r_i)}{j} X100 \qquad \textbf{(3.1)}$$

Where r_i is the residual error calculated with the experimental value as the basis and j is the number of data points available for every sample. The percentage ARE are listed in Table 3-VII. It can be seen from here that the langmuir model has the highest residual error while D-A model has the lowest possible residual error. This aptly buttresses the fact that has been presented above as a graphical comparison between the experimental datas and the theoretical models. The

%ARE values are comparitively close for both Langmuir and BET models describing their inability to account for adsorption in pores. Though D-R accounts for the filling of pores in coal the temperature invariant parameter n being constant prevents it from representing the experimental results accurately at high pressures. At lower pressure as seen for S-2 and S-3 the %ARE values of both D-R and D-A models are quite close to each other. The heterogenety of coal can been seen from the fact that even D-A equation which has a very low %ARE of 1.17% for S-5 has a higher %ARE of 5.30% for S-1 due to its inability to represent the sorption curve obtained experimentally. The values further suggest that the D-A equation is able to represent, more aptly the data

Table 3-VII: Percentage absolute residual errors (%ARE) for Langmuir, BET, D-R and D-A models

Sample	%ARE-Langmuir	%ARE-BET	%ARE-D-R	%ARE-D-A
S-1	15.68	15.91	16.20	5.30
S-2	2.26	2.79	1.09	1.35
S-3	3.56	3.71	2.69	2.75
S-5	8.45	8.66	9.57	1.17

obtained for samples S-1 and S-5 for which *n* value is closer to 1. For specimens S-2 and S-3 for which *n* values are to 2 it should also be noted that the %ARE values are lesser for D-R than those obtained for the D-A equation. The results obtained from Langmuir and BET models for S-2 and S-3 are substatiated by the corresponding %ARE values obtained. Thus, while D-A is capable perfectly representing S-1 and S-5 with a maximum of 6% error, Langmuir approximation of datas for S-2 and S-3 are more accurate with a maximum error of 4%. Even under these cases the TVFM based D-R and D-A represent the datas with deviation of not more than 3%.

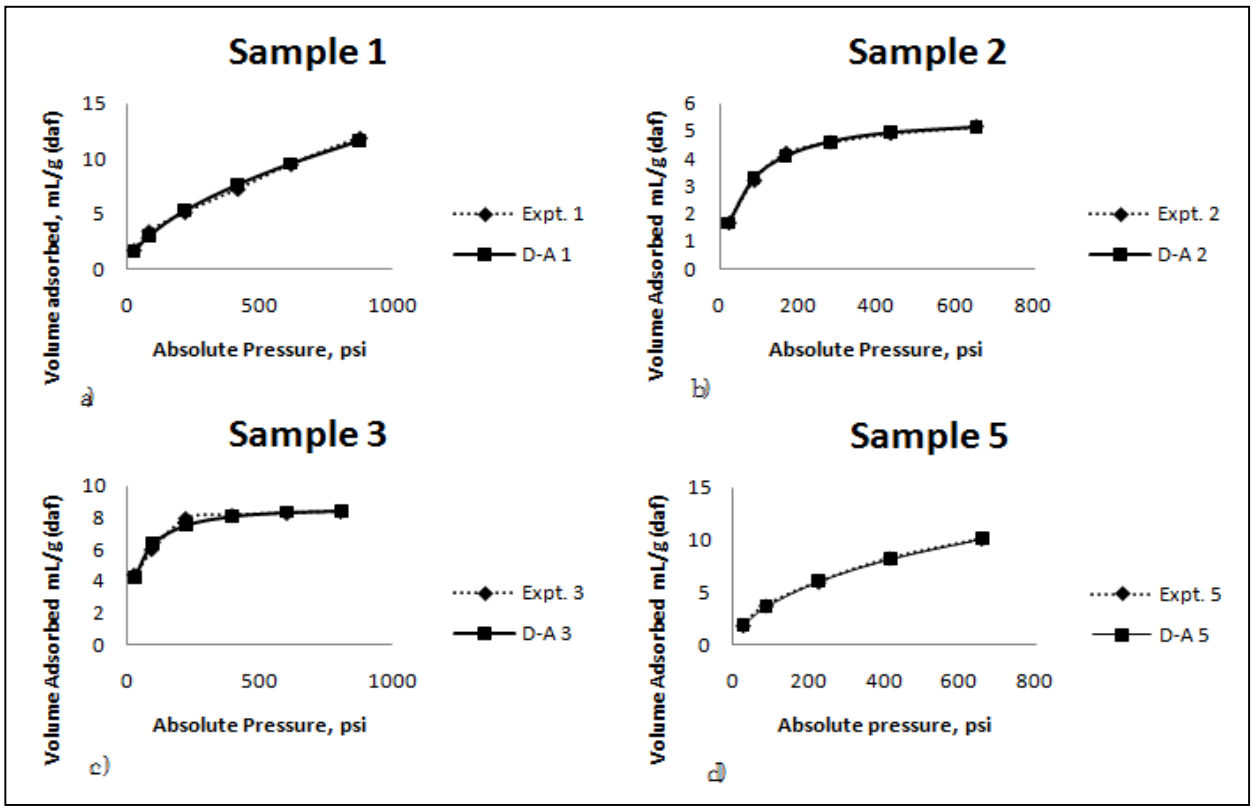

Figure 3-4: D-A model adsorption curves for 4 samples at 30°C

3.9 Absolute and Gibbs' values:

According to Gibbs, the magnitude of adsorption is defined as a certain excess quantity representing the difference between the quantity of adsorptive in a real adsorption system and in a hypothetical system characterised by the same macroscopic parameters of state as the real systems but, in which the coexisting phases are homogeneous all the way up to a certain mathematical interface [28]. Till now all studies that have been conducted are based on the Gibbs values of adsorbed gas volume. This does not take into into account the change in gas density due to the conditions of pressure and temperature that prevail during the adsorption of the gas on solid coal. While this density is taken into account, the values so obtained are called absolute values and are correspondingly found to be higher that the Gibb's values especially at higher pressures. This can be seen from the figure (Fig. 8). The relation between Gibb's and absolute number of moles adsorbed is given as shown by the equation below.

$$n_{abs} = \frac{n_{Gibbs}}{[1 - \frac{\rho_{gas}}{\rho_{sorbed}}]} \quad \textbf{(3.2)}$$

Here, the value of gas density in the adsorbed state is assumed to constant with change in equilibrium pressure and is given as $\rho_{sorbed} = 1.18 g/mL$. The value of ρ_{gas} is specific to the temperature and pressure at which the gas is adsorbed and also takes into account the compressibility factor to account for non-ideal behaviour of the gas at higher pressures. This value was calculated using Peng-Robinson EOS. Since, the procedure for calculation of volume of adsorbed gas involves the use of the Gibbs hypothesis of the excess gas adsorbed, the values hence calculated correpond to the value of excess Gibbs' moles adsorbed given by n_{Gibbs}. The comparison between the volume calculated from the Gibbs and absolute values is shown below (Fig. 3-3). Further more though the isotherms have been formulated only for the Gibbs excess adsorbed values, they were also applied to the absolute values hence obtained and their *%ARE* was calculated and is given in Table IX. Since absolute values are higher than the Gibbs values, the corresponding *%ARE* values were are also calculated to be higher than their Gibbs' counterparts. It could also be deciphered from the figure that the absolute adsorption curve follows a similar trend to that of the Gibbs excess adsorption curve upto a certain euilibrium pressure after which the absolute curve has a higher slope than the Gibbs curve. From all the said graphs, this equilibrium pressure upto which the curves have equal slopes was found to be in the range of 250-300 psig. Thus, the absolute values follow the same trend as the Gibbs values in case of the *%ARE* values. The trends of absolute values for various adsorption isotherm model is shown in figures 3-6 through 3-9.

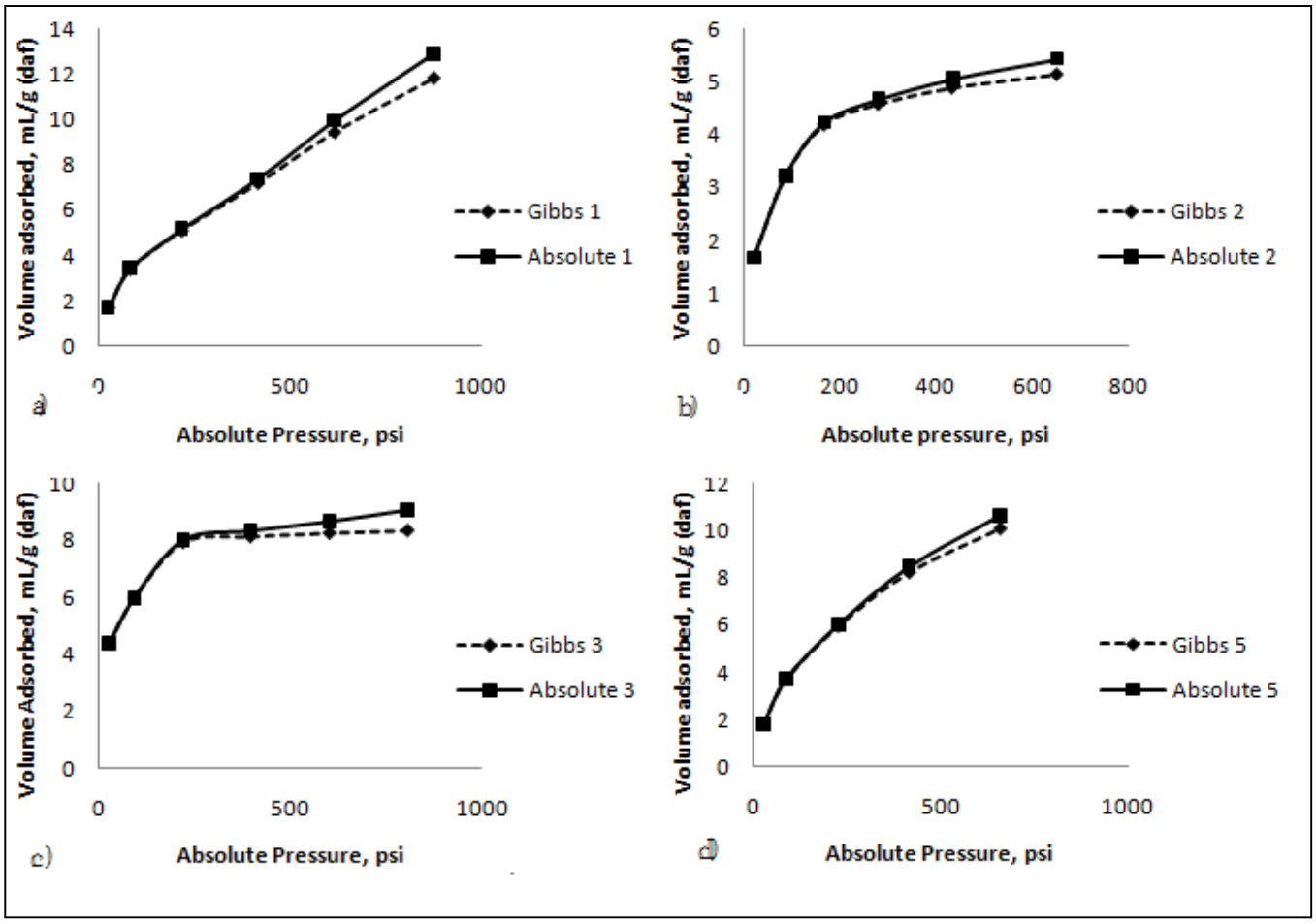

Figure 3-5: Comparison of Gibbs and Absolute adsorbed gas volume

Table 3-VIII: Percentage ARE values for Absolute Langmuir, BET, D-R and D-A isotherm models

Sample	%ARE-Langmuir	%ARE-BET	%ARE-D-R	%ARE-D-A
S-1	17.15	17.36	18.21	7.90
S-2	3.31	3.76	1.57	1.28
S-3	5.00	5.47	2.96	2.54
S-5	9.25	9.85	10.62	1.39

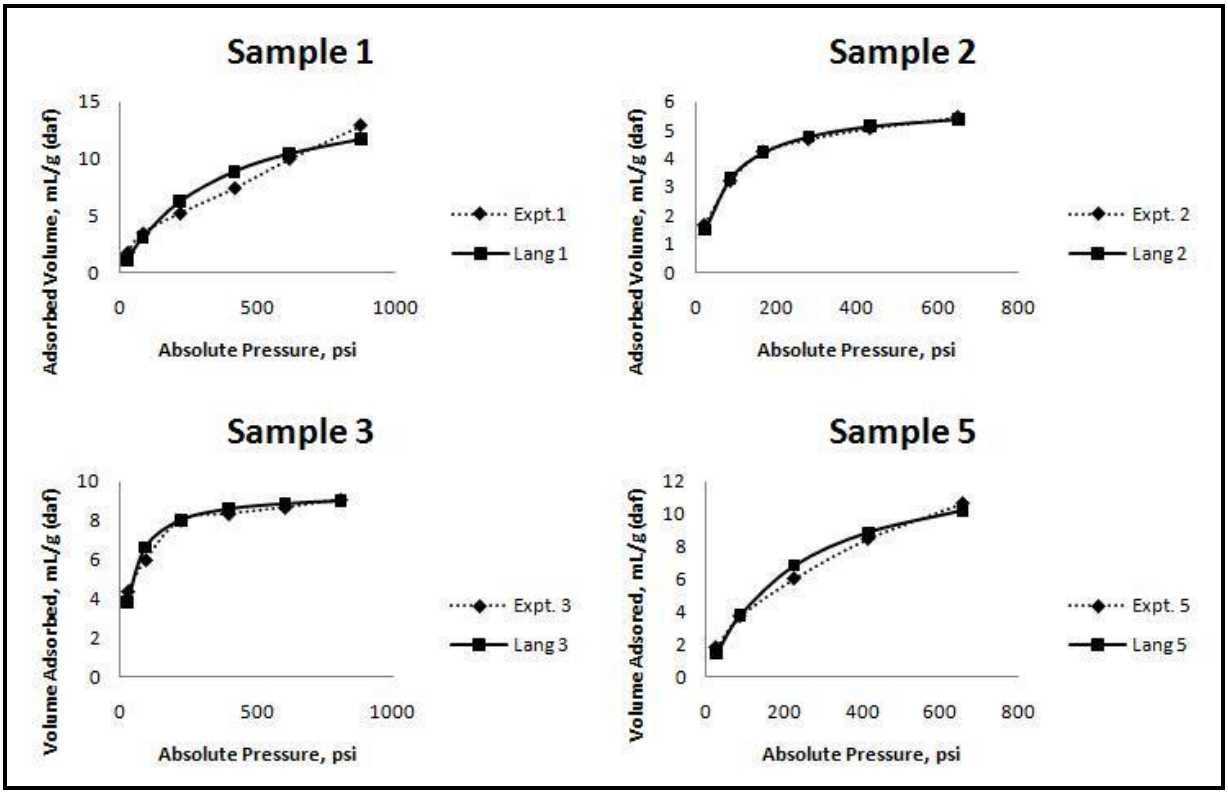

Figure 3-6: Absolute Langmuir adsorbed volumes

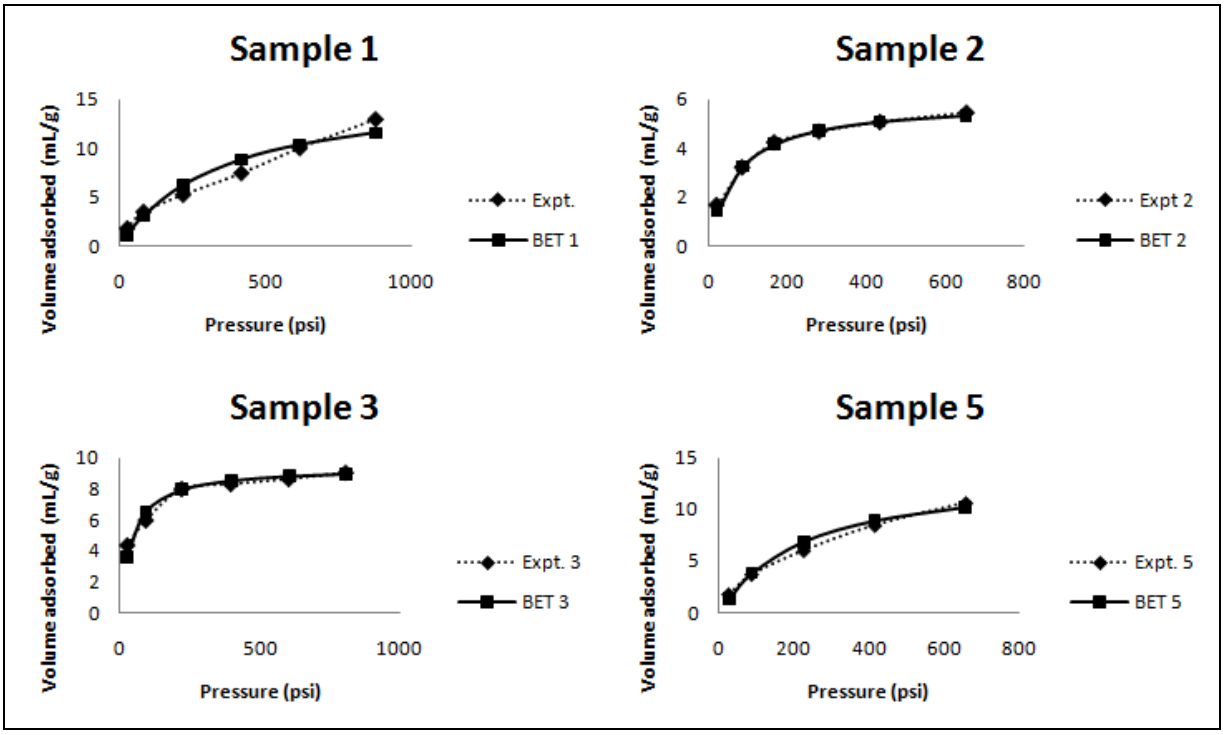

Figure 3-7: Absolute BET adsorbed volumes

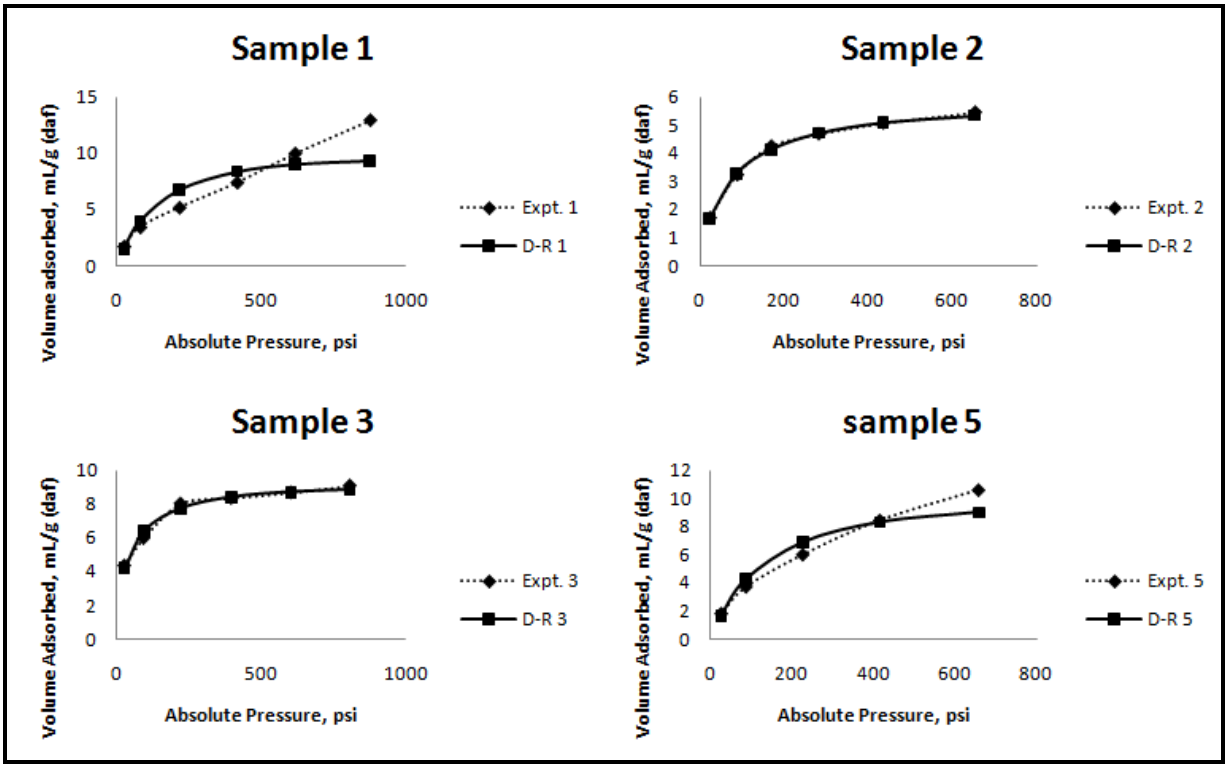

Figure 3-8: Absolute D-R adsorbed volumes

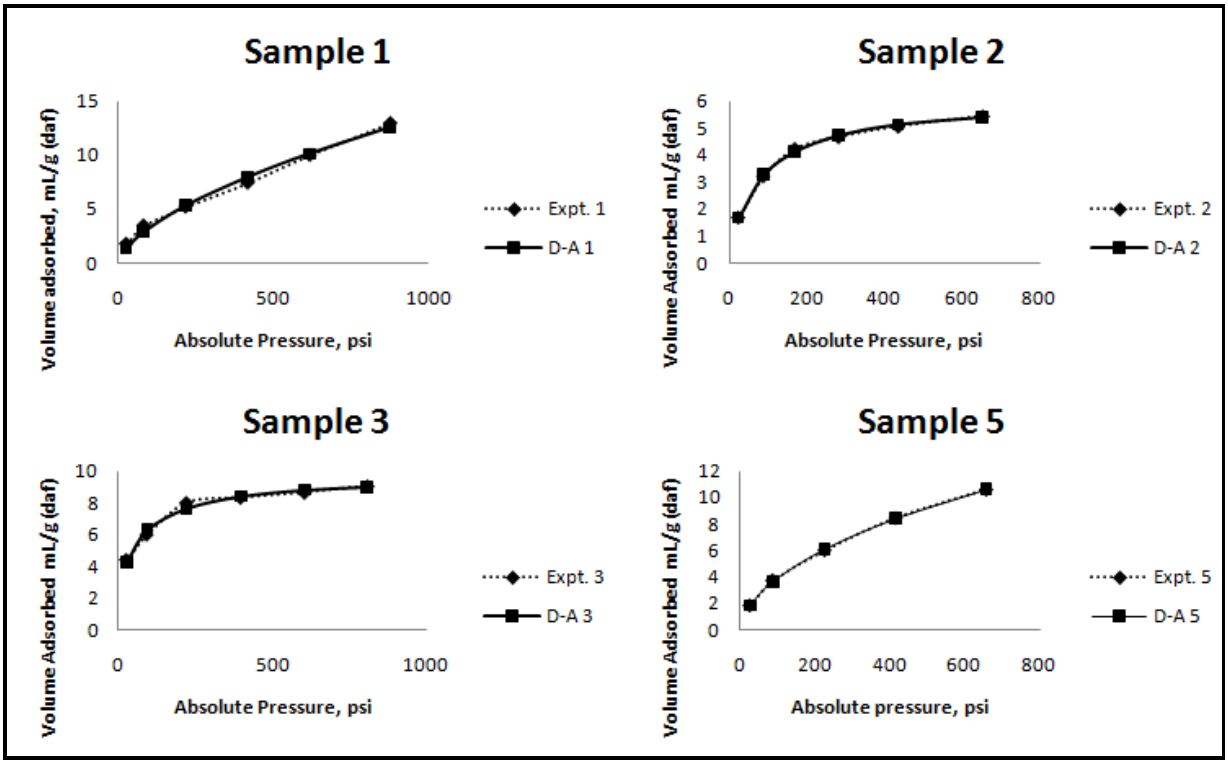

Figure 3-9: Absolute D-A adsorbed volumes

4.CONCLUSIONS

4 Conclusions

Carbon dioxide sorption studies were carried out on 4 samples obtained from Raniganj East CBM block of the Raniganj formation near Durgapur, India. This study revealed the incapability of the Langmuir model to represent the data accurately enough. The D-A model gave an adequately satisfactory representation suggesting that the pore filling model proposed by Polanyi in [12, 13] and Dubinin in [14, 16] is an accurate representation of gas adsorption in coals.

There exits a trend of coal rank, mineral matter, moisture, coal maturity with sorption capacity. The sample S-1 had the highest sorption capacity of 11.86mL/g (daf) under a pressure of 616psig and showed an increasing trend. While sample S-5 also showed a higher sorption capacity of 10.09mL/g (daf), it saturated at this point suggesting that this could be the maximum sorption capacity. Though there is an increasing trend in the adsorption capacity with seam depth, this does not essentially translate to a relation between adsorption capacity and other coal properties in spite of the fact that most of the coal properties conform to those given in [4]. The relation between the maceral composition and the adsorption capacity has not been studied for Raniganj coals though literature for certain other coals point to the fact of independence of adsorption from maceral composition. The coal adsorption capacity was also found to increase considerably with increase in pore size distribution parameter (D) of the D-A equation (ix). While S-1 had a D value of 0.562, that of S-5 was 0.422.

This data will help us to incorporate the values of model parameters to a simulator software to correctly predict the CO_2 sequestration potential of a seam and also help to estimate the ECBM recovery. The comparison of various models was done in order to enable the design of a simulator capable of simulating the sorption in the Raniganj coals from the available coal property data. On knowing which model best fits the experimental data, one can use the same to design the simulator to generate sortion data on feeding the necessary coal properties.

The gas content of the Raniganj East Block has been estimated to be 2-8m^3/t with a CBM potential of 42.48 billion m^3 [29]. Though studies with regards to the petrographic nature have

been carried out by Pareek in [30], their influence on gas sorption in coals and of the Raniganj formation in particular needs to be done inorder to support the above findings.

Other factors like pore swelling due to adsorption and coal seam permeability have not been taken into account during this study. A study [31] has confirmed that the values for CO_2 adsorption calculated under laboratory conditions varies significantly with that calculated during the field test for US coals. Since the experiments were carried out on crushed coal samples, the results may not be the same when performed in the field due to the various geological factors that would be involved. Seam permeability has been found to affect the flow of the sequestered CO_2. This could affect the retentivity of the gas in the seam. Further studies are also required to determine the exact temperature at which the sequestration process needs to be carried out. The behaviour of CO_2 and its adsorption characteristics on coal under both subcritical and supercritical conditions needs to be studied. A similar study has been conducted in [32] for Korean coals.

One of the major factors affecting actual site testing would be the temperature conditions pertaining to the area in which the coal seam exists. India, being a tropical country has temperatures close to an average of 30°C. The summer temperatures cross the 40°C mark. Under these temperature conditions CO_2 is in a supercritical state. This is one of the reasons why the adsorption behaviour of CO_2 on coal has to be studied under superctical conditions. The variations in coal properties and composition across the globe makes it difficult to draw a single conclusive result on the basis of studies conducted on coal from elsewhere.

Hence, it can be concluded that there i sn't a single property on the basis of which the feasibility of a coal seam for sequestration can be determined. Its also the case with determining the trend of sorption capacity from the trends of other properties like moisture or ash content. More studies as regards to dependance of adsorption capaction on the temperature and condition of the gas adsorbed need to be done. Under supercritical conditions the above said D-R has been proven to fail and a modified D-R equation has been proposed in [27] for this purpose. Desorption studies also need to be carried inorder to determine the exact time dependent retention capacity and capability of the said coal seam.

The cost estimate according to National Energy Technology Laboratory (NETL), Department of Energy (DOE), USA for sequestering one ton of CO_2 has been $30. Assuming this value doesn't change with the country for the same technology used, additional monitoring costs of $0.1-$0.3 are incurred by the power plant implementing CCS. This results in a overall energy burden of 40-50% to the company. This results in the energy production costs suffering an increase of 30-60%. The DOE has also estimated that with EOR, the merit could be in the range of $10-$16 per ron of CO_2 sequestered.

Indian Raniganj coals as stated above have a relatively high CBM potential and gas content. This is one of the prime reasons to explore the possibility of CO_2 in the Raniganj seams. With this potential, the sequestration process could become economically viable along with ECBM.

Thus, this study is still not conclusive enough to determine the feasibility for CO_2 sequestration in the Raniganj coals of India.

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